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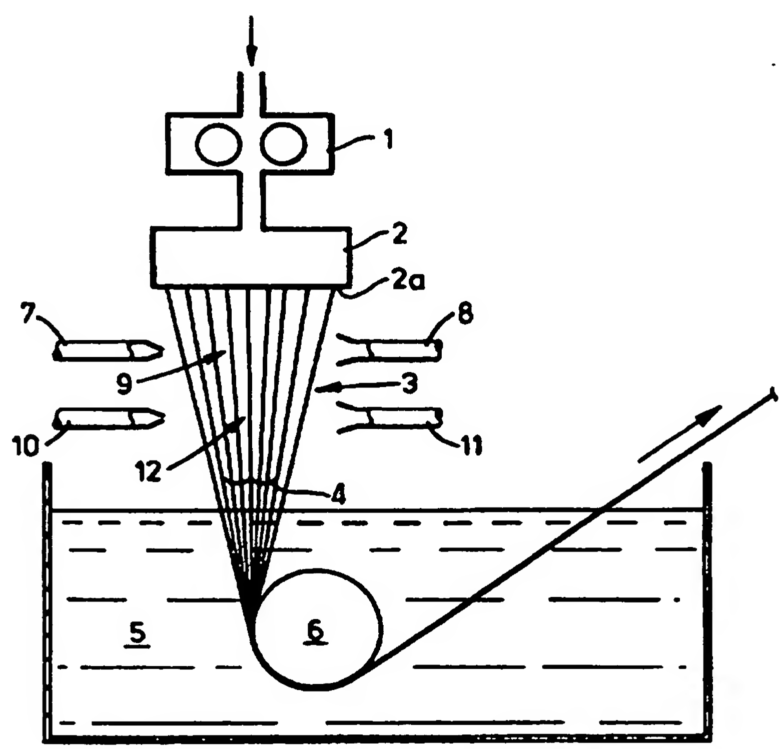
(57) Abstract

A method of manufacturing extruded articles of lyocell is described wherein a solution of cellulose in a tertiary amine N-oxide is extruded by way of a die (2) through an air-gap (3) into a coagulating bath (5), air being supplied to and discharged from the air-gap (3), characterised in that the air-gap (3) comprises a first region (9) adjacent the face (2a) of the die (2) and a second region (12) more remote from the face (2a) of the die (2), the moisture content of the air supplied to the first region (9) being maintained at a lower value than the moisture content of the air supplied to the second region (12). The method provides improved spinnability and may provide lyocell filaments with a reduced tendency to fibrillation.



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MANUFACTURE OF EXTRUDED ARTICLES

Field of the invention

This invention relates to methods of manufacturing cellulose articles in which a solution of cellulose in a tertiary amine N-oxide is extruded by way of a die into a coagulating bath.

It is known that cellulose can be dissolved in certain tertiary amine N-oxides (which may for convenience also be called amine oxides) to form a solution or dope which can be extruded by way of a die into a coagulating bath to form shaped articles such as fibres and films. The dope generally contains a small proportion of water, and the coagulating bath is usually an aqueous bath. The coagulated article is then washed to remove residual amine oxide therefrom. This process is an example of a solvent-spinning process, and fibre so produced may be called solvent-spun cellulose fibre or lyocell fibre. An example of a suitable amine oxide solvent is N-methylmorpholine N-oxide (NMMO).

Background art

US-A-4,261,943, the contents of which are incorporated herein by way of reference, describes such a solvent-spinning process wherein a solution of cellulose in aqueous NMMO is extruded by way of a spinnerette through an air-gap, for example 5 or 30 cm in length, to form filaments which then pass into a water bath, thereby producing lyocell fibre. This patent also describes a solvent-spinning process wherein the filaments in the air-gap are coated with a nonsolvent liquid for cellulose, for example water, immediately after extrusion. This is said to reduce the tendency of the filaments to fuse together in the air-gap.

WO-A-93/19230 describes a solvent-spinning process wherein the filaments in the air-gap are cooled before introduction into the coagulating bath, for example by subjecting them to a current of cold air. The temperature of

the dope may be 90 to 110°C, the temperature of the cooling air -5 to +5°C, and the length of the air-gap 60 to 145 mm.

Disclosure of invention

According to the present invention there is provided a method of manufacturing extruded articles of lyocell wherein a solution of cellulose in a tertiary amine N-oxide is extruded by way of a die through an air-gap into a coagulating bath, air being supplied to and discharged from the air-gap, characterised in that the air-gap comprises a first region adjacent the face of the die and a second region more remote from the face of the die, the moisture content of the air supplied to the first region being maintained at a lower value than the moisture content of the air supplied to the second region.

The extruded lyocell articles may take the form of films or, preferably, filaments (including not only tows of filaments which may subsequently be cut to form staple fibre but also continuous filament yarns). When the articles are filaments, the die is commonly called a spinnerette, and the process of extrusion is commonly called spinning.

The length of the air-gap between the die and the coagulating bath is preferably in the range 10 to 160 mm, more preferably 15 to 100 mm or 20 to 60 mm. It will be understood that, although the gas in the air-gap is preferably air, other inert gases or gas mixtures, for example nitrogen, may be used.

The two regions of the air-gap may be of the same or different lengths. In one embodiment, which may be preferred, the length of the first region is less than the length of the second region. The first region is preferably 3 to 10 mm in length so that the second region occupies the remaining longer portion of the air-gap.

The cellulose solution (which may also be called a dope)

is conventionally extruded downwardly through the air-gap. Air is preferably supplied to and extracted from the air-gap in a direction substantially transverse to the direction of travel of the dope extrudate through the air-gap, that is to say horizontally when using such conventional extrusion techniques. In such a transverse arrangement, the current of air flowing across the air-gap may conveniently be referred to as a cross-draft. The velocity of the air supplied to the air-gap in both regions is preferably in the range 1 to 20 m/sec, more preferably 2 to 10 m/sec. It will be appreciated that the velocity of the air should be high enough to maintain different atmospheric conditions around the dope extrudate within the two different regions of the air-gap, but not so high as to disrupt the orderly passage of the dope extrudate therethrough. In general, higher velocities may cause such disruption in longer air-gaps. The velocity of the air in the first and second regions of the air-gap may be the same or different. Suitable air velocities can be determined in any particular case by simple trial.

Methods of discharging air from either or both regions can be by extraction. Air can conveniently be supplied to and extracted from the air-gap by suitably designed blowing and suction nozzles. It will be understood that separate blowing nozzles are required for each of the first and second regions. There may be one or more suction nozzles. In a preferred embodiment, each blowing nozzle faces towards a suction nozzle of similar dimensions thereto. This has the advantage that it permits closer control of the atmospheric conditions around the dope extrudate across each region of the air-gap; particularly in the first region if, as may be preferred, the length of the first region is less than the length of the second region.

The temperature of the air supplied to the air-gap is generally around ambient temperature, for example in the range 0 to 40°C, often 20 to 30°C. The temperature of the dope supplied to the die is commonly in the range of about

80-125°C, and the air flow accordingly serves to cool the extrudate in the air gap. According to conventional practice, the take-up velocity of the extruded article from the coagulation bath is higher than the extrusion velocity of the dope through the die, often by about a factor in the range 2.5 to 25, so as to stretch the extrudate with the purpose of improving its mechanical properties. It is thought that such stretching occurs almost entirely within the air-gap. Cooling the extrudate in the air-gap often restricts the zone in which stretching occurs to the portion of the air-gap closest to the face of the die. In the method of the invention, it may be preferred that substantially all the stretching occurs within the first region of the air-gap. The take-up velocity of the extruded article is preferably in the range 5 to 100 m/min.

The moisture content of the air supplied to the second region of the air-gap is preferably in the range of about 1 to 30 g, more preferably 10 to 20 g, water per kg air greater than the moisture content of the air supplied to the first region. The moisture content of the air supplied to the first region is preferably in the range 0 to 20, more preferably 0 to 10, g water per kg air, and the moisture content of the air supplied to the second region is preferably in the range 5 to 30 g water per kg air.

Lyocell fibres commonly exhibit a tendency to fibrillate, particularly when subjected to mechanical stress during hot wet processing treatments such as those commonly encountered during fabric manufacture, for example scouring, bleaching and dyeing. On fibrillation, long fibrils become partially detached from the surface of the fibre, giving the individual fibres (as well as yarns and fabrics containing them) a hairy appearance which may be aesthetically unpleasing. It has surprisingly been found that fibre produced by the method of the invention may exhibit a lower tendency towards fibrillation than fibre produced by conventional fibre spinning techniques.

It is known in lyocell spinning that the dope extrudate, for example in the form of filaments, may on occasion break in the air-gap. This type of breakdown may be referred to as loss of spinning stability or as poor spinnability. Evidence of poor spinnability may be provided by observation of broken or stuck filaments in the collected product or in severe cases by complete breakdown of spinning in the air-gap or coagulation bath. It has surprisingly been found that the method of the invention provides better spinning stability than conventional techniques, especially at longer air-gaps. Although this effect is difficult to quantify, it can readily be confirmed by observation.

The average degree of polymerisation (D.P.) of the cellulose in the dope may generally be in the range 250 to 2000, and is preferably in the range 500 to 2000, further preferably 750 to 1000. It has been observed that good spinnability can be obtained over a wide range of conditions when cellulose D.P. is in the range 750 to 1000. The degree of polymerisation (D.P.) of cellulose is conveniently assessed by viscosimetry of a dilute solution of cellulose in an aqueous metal/amine complex solvent, for example cuprammonium hydroxide solution. A suitable method, based on TAPPI Standard T206, is described hereinafter as Test Method 3. Cellulose D.P. is a measure of the number of anhydroglucose units per molecule. It will be understood that D.P. measured in this manner is a viscosity average D.P.

<u>Brief description of drawing</u>

The invention will now be more particularly described with regard to the accompanying drawing, which is a schematic illustration of apparatus suitable for carrying out the invention.

Referring to the drawing, a solution of cellulose in aqueous amine oxide is fed by way of a gear pump 1 to a

spinnerette 2. The dope may for example contain 5 to 25% by weight cellulose, 70 to 85% by weight NMMO and 5 to 15% by weight water, and the temperature of the dope may be in the range 80 to 125°C. The dope is extruded downwardly through the holes in the spinnerette 2 into an air gap 3 maintained at a temperature below that of the dope, where it solidifies to form a bundle of filaments 4. The filaments 4 then pass into an aqueous coagulating bath 5, pass partly around a roller 6 and are withdrawn for washing, drying and other conventional processing operations. The surface speed of the roller 6 is higher than the velocity of the dope issuing through the holes of the spinnerette 2 so as to stretch the filaments 4. Stretching of the filaments occurs largely within the air gap 3.

A first supply of air is blown into the air-gap 3 in a first region 9 adjacent the spinnerette 2 from a blowing nozzle 7 and extracted from the air-gap 3 by a suction nozzle 8, so that it passes through the air-gap 3 transversely to the direction of travel of the filaments 4. The nozzles 7, 8 are so arranged that this procedure serves to maintain the temperature and humidity of the atmosphere in the first region 9, which lies adjacent the face 2a of the spinnerette 2, at desired values. A second supply of air is similarly blown into the air-gap 3 in a second region 12 remoter from the spinnerette 2 from a blowing nozzle 10 to a suction nozzle 11. The nozzles 10, 11 are so arranged that this procedure serves to maintain the temperature and humidity of the second region 12, situate between the first region 9 and the coagulating bath 5, at desired values. The nozzles 7 and 10 extend to supply air across the entire bundle 4 of filaments. The moisture content of the air supplied to blowing nozzle 7 is lower than that supplied to blowing nozzle 10. The temperatures of the two supplies of air may be the same or different.

Although the drawing illustrates the supply of two different qualities of air into the air-gap, it will be

understood that three or more different qualities of air may be so supplied into different regions of the air-gap without departing from the spirit of the invention.

The fibrillation tendency of lyocell fibre may be assessed by the following Test Methods:

__Test Method 1 (Sand Test)__

A small tuft of fibre containing 100 to 200 filaments is cut to 5 mm lengths. These short fibres are placed in a 20 ml phial containing 4 g of glass micro-beads, and 8 ml water is added. The phial is securely stoppered and shaken on a Stewart flask shaker at 2800 cycles/min for 20 min.

A few fibres are removed and placed on a microscope slide. The fibrillation index (C_f) is calculated from optical micrographs of the fibrillated fibres. The total lengths of the fibrils, f, attached to a length of fibre, L, are measured. The fibrillation index is given by the equation:

$$C_f = \Sigma f/L$$

This operation can be carried out manually or by image analysis. Alternatively, a set of standard micrographs can be set up for comparison. Trained fibre technologists have been found to be consistent in their assessment with this method. In practice, it is impossible to measure a fibrillation index above about 30, owing to the difficulty in seeing the large number of fibrils. Data are measured on the middle of the 5 mm length of fibre and on the end. Experience shows that the result for the fibre end correlates best to fabric performance, and only this is the figure quoted herein as C_f (TM1).

Test Method 2 (Scour-dye)

The following method was used to assess Fibrillation Index (F.I.). Samples of fibre were arranged into a series showing increasing degrees of fibrillation. A standard length of fibre from each sample was then measured and the number of fibrils (fine hairy spurs extending from the main body of the fibre) along the standard length was counted. The length of each fibril was measured, and an arbitrary number, being the product of the number of fibrils multiplied by the average length of each fibril, was determined for each fibre. The fibre exhibiting the highest value of that arbitrary number was identified as being the most fibrillated fibre and was assigned an arbitrary Fibrillation Index of 10. A wholly unfibrillated fibre was assigned a Fibrillation Index of zero, and the remaining fibres were ranged from 0 to 10 based on the microscopically measured arbitrary numbers.

The measured fibres were then used to form a standard graded scale. To determine the Fibrillation Index for any other sample of fibre, five or ten fibres were visually compared under the microscope with the standard graded fibres. The visually determined numbers for each fibre were then averaged to give a Fibrillation Index for the sample under test. It will be appreciated that visual determination and averaging is many times quicker than measurement, and it has been found that skilled fibre technologists are consistent in their rating of fibres.

The Fibrillation Index of fabrics can be assessed on fibres drawn from the surface of the fabric. Woven and knitted fabrics having an F.I. of more than about 2.0 to 2.5 exhibit an unsightly appearance.

A tow of 1.7 dtex lyocell fibres was crimped and cut to form 30 mm staple fibre, which was spun into 20 tex yarn. The yarn was knitted into an 80 mm wide stockinette, which

was scoured and dyed to a navy blue shade. The knitted fabric was washed at 40°C in a domestic washing machine and dried in a domestic tumble dryer. The Fibrillation Index (F.I.) was measured on fibres drawn from the surface of the dry fabric either after scouring and dyeing or after one or more wash/tumble (W/T) cycles.

<u>**Test Method 3 - Measurement of Cuprammonium Solution Viscosity and D.P.**</u>

This test is based on TAPPI Standard T206 os-63. Cellulose is dissolved in cuprammonium hydroxide solution containing 15±0.1 g/l copper and 200±5 g/l ammonia, with nitrous acid content < 0.5 g/l (Shirley Institute standard) to give a solution of accurately-known cellulose concentration (about 1%). Solution flow time through a Shirley viscometer at 20°C is measured, from which viscosity may be calculated in standard manner. Viscosity average D.P. is determined using the empirical equation:

$$D.P. = 412.4285 \ln [\ 100(t-k/t)\ /\ n.C\ ] - 348$$

where t is flow time in seconds, k the gravity constant, C the tube constant and n the density of water in g/ml at the temperature of the test (0.9982 at 20°C).

The invention is illustrated by the following Examples, in which parts and proportions are by weight except where otherwise indicated.

<u>**Example 1**</u>

A spinning dope was prepared containing woodpulp cellulose (various proportions; various degrees of polymerisation (D.P.)) specified below, 74-80% NMMO and 7.5-12.6% water. This was extruded by way of a spinnerette (head temperature 115°C) containing 95 holes each 80 micron in diameter through an air-gap of length specified below into

temperature 115°C) containing 95 holes each 80 micron in diameter through an air-gap of length specified below into a coagulating bath comprising 25% NMMO and 75% water at 25°C to form lyocell fibre. Air was blown transversely across the extruded filaments from upper and lower supplies. The depth of the first, upper region of these cross-drafts was approximately 4 mm. The second, lower cross-draft was produced by directing an air flow from a hand-held electric blower through a shaped funnel. The moisture content of the lower cross-draft was increased where desired by bleeding a small amount of low pressure steam into the air supply at the entrance to the funnel to increase relative humidity (R.H.). The fibre was washed with water to remove residual NMMO and dried. It was then assessed for fibrillation tendency using Test Method 1. Samples of fibre were cut to form staple fibre which was spun into yarn. Yarn quality was assessed visually on a scale of 1 (very poor) to 5 (very good). Experimental details and results are presented in Table 1:

Table 1

Cellulose %	Cellulose D.P.	Yarn quality	C_f(TM1)	Filament sticking
Spinning speed 60 m/min; air-gap 20 mm; upper air-supply (first region) 20°C/0% R.H.; lower air-supply (second region) 20°C/40% R.H.				
15	850	4	5.5	No
15	630	5	6.5	No
15	472	5	9.4	No
12.5	630	4	5.9	No
10	850	4	5.3	No

Spinning speed 30 m/min; air-gap 75 mm; upper air-supply (first region) 20°C/0% R.H.; lower air-supply (second region) 20°C/40% R.H.

15	850	4	6.6	No
15	630	5	4.9	No
15	472	4	3.3	Some
12.5	630	3	4.1	Some
10	850	4	4.2	No

Spinning speed 30 m/min; air-gap 150 mm; upper air-supply (first region) 20°C/40% R.H.; lower air-supply (second region) 30°C/60% R.H.

15	850	3	3.2	Some
15	630	3	0.0	Little
15	472	2	0.1	Yes
12.5	630	1	0.0	Yes
10	850	1	2.5	Yes

Spinning speed 10 m/min; air-gap 150 mm; upper air-supply (first region) 20°C/0% R.H.; lower air-supply (second region) 20°C/40% R.H.

15	850	4	3.8	Little
15	630	2	1.3	Severe
15	472	2	0.0	Some
12.5	630	1	0.7	Yes
10	850	1	3.5	Yes

Spinning speed 10 m/min; air-gap 75 mm; upper air-supply (first region) 20°C/40% R.H.; lower air-supply (second region) 30°C/60% R.H.

15	850	4	0.0	No
15	630	3	1.5	Minimal
15	472	2	0.0	Yes
12.5	630	1	2.1	Yes
10	850	1	4.8	Yes

Example 2

Example 1 was repeated, except that the dope contained 15.2% woodpulp cellulose (D.P. 600), 75% NMMO and 9.8% water. The fibre so produced was assessed for fibrillation tendency using Test Methods 1 and 2. Experimental details and results are presented in Table 2:

Table 2

Air °C/R.H. % Upper	Lower	Spin quality	C_f (TM1)	Filament sticking	F.I. (TM2) Scour/dye	IW/T
Spinning speed 60 m/min; air-gap 20 mm						
-	20/40	5	11.0	No	4.7	5.5
-	30/60	5	9.0	No	4.7	6.0
Spinning speed 30 m/min; air-gap 150 mm						
-	30/60	3.0	0.1	Yes	1.7	4.1
20/40	30/60	2.7	1.7	Yes	1.9	1.9
Spinning speed 10 m/min; air-gap 75 mm						
-	30/60	3.3	3.6	Some	2.5	3.5
60/40	30/60	4.0	0.7	No	1.0	2.0
Spinning speed 10 m/min; air-gap 150 mm						
-	20/40	1.3	1.2	Severe	-	
20/0	20/40	2.0	3.1	Yes	2.7	5.2

The experiments with a 20 mm air-gap were conducted with spinning head temperature 110°C. The experiments with longer air-gaps were performed with spinning head temperatures of 90, 100 and 110°C; little difference was observed between the results, and they have been averaged.

Example 3

Example 1 was repeated, except that the temperatures and relative humidities of the upper air supply were 20°C and 40% and of the lower air supply were 30°C and 60%. Other experimental details and results are presented in Table 3:

Table 3

Cell D.P	Cell %	Spinning speed m/min	Air gap mm	Air Velocity m/sec	Tow tension	Spinning stability	C_f
630	15	10	20	2	44	Good	3.8
630	15	10	20	8	53	Good	1.9
630	15	10	40	2	25	Poor	0.0
630	15	10	40	8	52	Good	0.0
630	15	10	80	2	45	Good	0.0
630	15	20	20	2	100	Good	7.1
630	15	20	20	8	165	Good	6.4
630	15	20	40	2	80	Poor	5.8
630	15	20	40	8	148	Good	3.0
630	15	20	80	2	69	OK	2.1
630	15	40	20	2	120	V Good	10.6
630	15	40	20	8	150	V Good	9.5
630	15	40	40	2	150	V Good	6.2
630	15	40	40	8	225	V Good	6.0
630	15	40	80	2	126	Good	5.4

Cell D.P	Cell %	Spinning speed m/min	Air gap mm	Air Velocity m/sec	Tow tension	Spinning stability	C_f
850	13	10	20	2	57	V Good	5.1
850	13	10	20	8	84	V Good	3.0
850	13	10	40	2	65	OK	2.2
850	13	10	40	8	151	Good	0.2
850	13	20	20	2	110	V Good	5.5
850	13	20	20	8	117	V Good	1.0
850	13	20	40	2	90	Good	4.5
850	13	20	40	8	256	Good	6.0
850	13	40	20	2	140	V Good	8.9
850	13	40	20	8	170	V Good	6.8
850	13	40	40	2	130	Good	7.1
850	13	40	40	8	340	Good	6.0
850	13	40	80	2	110	OK	5.4

Cell D.P	Cell %	Spinning speed m/min	Air gap mm	Air Velocity m/sec	Tow tension	Spinning stability	C_f
850	15	10	20	2	240	V Good	2.7
850	15	10	20	8	650	Good	1.4
850	15	10	40	2	250	V Good	0.0
850	15	10	40	8	920	Poor	1.3
850	15	10	80	2	220	Good	0.6
850	15	10	160	2	310	OK	0.0
850	15	20	20	2	300	V Good	5.8
850	15	20	20	8	900	Poor	6.0
850	15	20	40	2	220	V Good	2.4
850	15	20	40	8	900	Poor	2.0
850	15	20	80	2	220	V Good	0.2
850	15	20	80	8	280	Good	0.2
850	15	40	20	2	460	V Good	4.6
850	15	40	20	8	1000	Poor	5.8
850	15	40	40	2	290	V Good	5.4
850	15	40	40	8	800	OK	5.0
850	15	40	80	2	210	V Good	0.0

Tow tension is an arbitrary number, higher values indicating higher tensions. Some stuck filaments were observed on occasion with the longer air-gaps, particularly at the higher air velocity.

Example 4

A spinning dope was prepared containing 13% cellulose (average D.P. 800), 75% NMMO and 12% water. It was extruded downwardly through a spinnerette,having 18,400 holes each 70 micron in diameter clustered in three parallel rows each about 1 m long (dope temperature 83°C), through a 30 mm air-gap into a coagulating bath containing 25% NMMO and 75% water to form a tow of lyocell filaments. Two supplies of air were blown transversely across the tow, the upper supply at a velocity of 12 m/sec from a 5 mm blowing nozzle disposed immediately adjacent the spinnerette and the lower supply at 9 m/sec from a 25 mm blowing nozzle disposed over the lower portion of the air-gap. Air was extracted through suction nozzles arranged in opposition to the respective blowing nozzles at the same velocities. The temperature of the upper (relatively dry) air supply was 20°C and its relative humidity was 40% (dew point 6°C). The temperature of the lower (relatively moist) air supply was 28°C and its relative humidity was 78% (dew point 24°C). Spinning quality and stability were good. The upper air supply was then turned off. Spinning quality immediately became poor, and it was necessary rapidly to reinstate the upper air-jet in order to avoid breakdown of the tow (loss of spinning stability) in the coagulation bath.

CLAIMS

1. A method of manufacturing extruded articles of lyocell wherein a solution of cellulose in a tertiary amine N-oxide is extruded by way of a die through an air-gap into a coagulating bath, air being supplied to and discharged from the air-gap, characterised in that the air-gap comprises a first region adjacent the face of the die and a second region more remote from the face of the die, the moisture content of the air supplied to the first region being maintained at a lower value than the moisture content of the air supplied to the second region.

2. A method according to claim 1, characterised in that the length of the air-gap is within the range 10 to 160 mm, preferably 20 to 60 mm.

3. A method according to claim 1 or claim 2, characterised in that the length of the first region is less than the length of the second region.

4. A method according to claim 3, characterised in that the length of the first region is within the range 3 to 10 mm.

5. A method according to any one of the preceding claims, characterised in that the velocity of the air supplied to each of the first region and second region is within the range 1 to 20, preferably 2 to 10, m/sec.

6. A method according to any one of the preceding claims, characterised in that the air is supplied into the first region and into the second region in a direction substantially transverse to the direction of travel of the extrudate through the air-gap.

7. A method according to any one of the preceding claims, characterised in that air is supplied into the air-gap into the first region and the second region by means of blowing nozzles, which are separate for the two regions.

8. A method according to claim 7, characterised in that air is discharged from the air-gap by means of a single suction nozzle facing towards the blowing nozzles.

9. A method according to claim 7, characterised in that air is discharged from the air-gap by means of separate suction nozzles facing towards each of the separate blowing nozzles and of similar dimensions thereto.

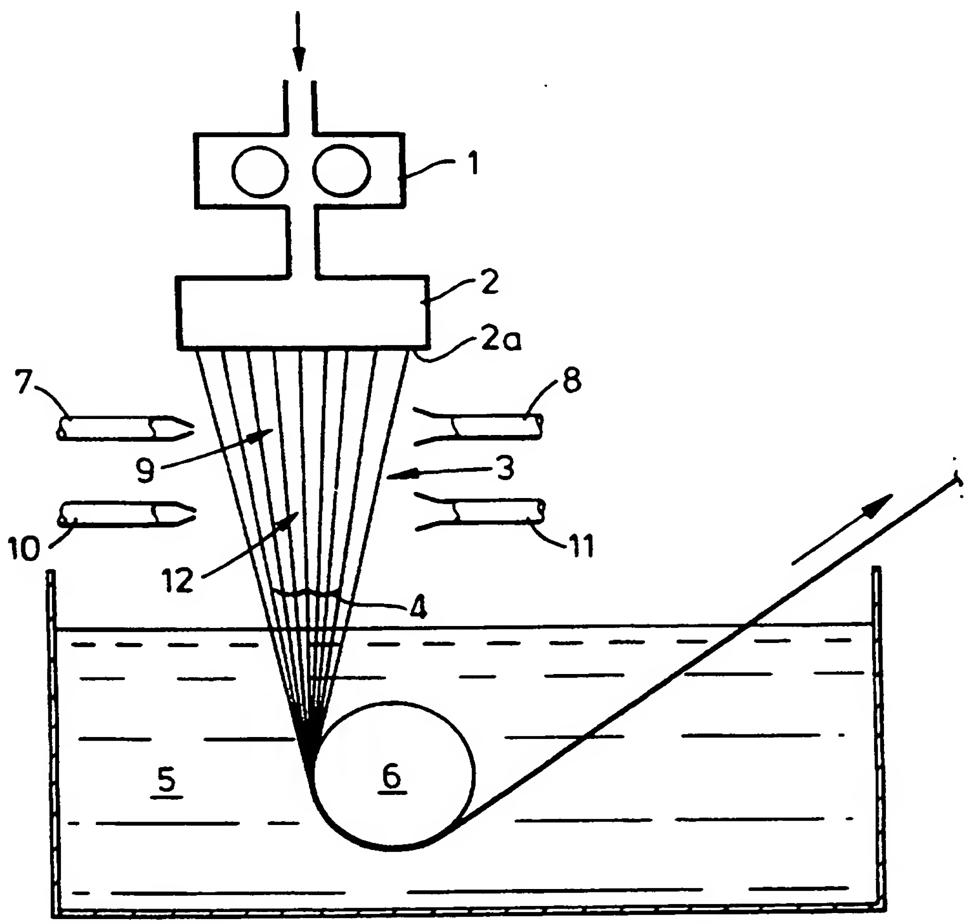
10. A method according to any preceding claim, characterised in that the moisture content of the air supplied into the second region is higher than that of the air supplied into the first region by a value within the range 1 to 30, preferably 10 to 20, g water per kg air.

11. A method according to any preceding claim, characterised in that the moisture content of the air supplied into the first region is within the range 0 to 20, preferably 0 to 10, g water per kg air.

12. A method according to any preceding claim, characterised in that the moisture content of the air supplied into the second region is within the range 5 to 30 g water per kg air.

13. A method according to any preceding claim, characterised in that the average degree of polymerisation of the cellulose in the solution is within the range 750 to 1000.

14. A method according to any preceding claim, characterised in that the extruded article is in the form of filaments of lyocell.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INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 96/00030

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 D01F2/00 D01D5/06 D01D5/088

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 D01F D01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,93 19230 (CHEMIEFASER LENZING AG) 30 September 1993 cited in the application see claims 1-5 ---	1-14
A	WO,A,94 28218 (COURTAULDS FIBRES HOLDINGS LTD) 8 December 1994 see claims 1-13,25,30,35,43-46 ---	1-14
P,A	WO,A,95 01470 (CHEMIEFASER LENZING AG) 12 January 1995 ---	
P,A	WO,A,95 04173 (CHEMIEFASER LENZING AG) 9 February 1995 -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

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Date of the actual completion of the international search	Date of mailing of the international search report
25 April 1996	14.05.96

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Tarrida Torrell, J

INTERNATIONAL SEARCH REPORT

national Application No
PCT/GB 96/00030

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